

Structural Trends Interpretation of the Metal-to-Semiconductor Transition in Deformed Carbon Nanotubes

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(Dated: February 2, 2008)

Two mechanisms that drive metal-to-semiconductor transitions in single-walled carbon nanotubes are theoretically analyzed through a simple tight-binding model. By considering simple structural trends, the results demonstrate that metal-to-semiconductor transitions can be induced more readily in metallic zigzag nanotubes than in armchair nanotubes. Furthermore, it is shown that both mechanisms have the effect of making the two originally equivalent sublattices *physically* distinguishable.

PACS numbers: 72.80.Rj, 73.23.-b, 73.22.-f, 85.35.Kt

Carbon nanotubes are promising candidates for the next generation of nanometer-scale electronic devices due to their unique electronic properties.[1, 2] As the electronic properties of an ideal carbon nanotube are uniform throughout the structure, the key problem for electronic device development is to control or tailor the electronic properties of a given nanotube.

Experimentally, atomic force microscope tips are used to manipulate single-walled carbon nanotubes (SWNTs).[3] The results show that mechanical deformation of SWNTs may lead to a metal-to-semiconductor transition (MST) in their electronic properties. This experiment suggests a means for SWNT-based electronic devices: a metallic SWNT can act as a good conducting lead, and when mechanical deformation leads to semiconducting areas along the tube a nanometer-scale electronic device is produced. Thus, understanding MSTs in SWNTs is a necessary step in realizing nanotube based electronic devices.

Theoretically, many studies consider the MST in SWNTs. Park *et al.* point out that the breaking of the mirror symmetry leads to a MST in armchair SWNTs.[5] Lammert *et al.* compare the squashed armchair SWNTs to graphene bilayers and explain the MST in squashed armchair SWNTs through the interaction between graphene bilayers.[6] For metallic zigzag SWNTs, all the studies agree that the MST is driven by the curvature effect.[5, 6]

In the authors' previous work,[4] the MST in squashed armchair SWNTs is explored. It is shown that when a structural perturbation is made the two original equivalent sublattices in the armchair SWNTs become distinguishable, and an energy gap opens, leading to a MST. It is also pointed out that the *physical* distinction of the two sublattices in armchair SWNTs could be achieved by a combined effect of mirror symmetry breaking and bond formation between the flattened faces of the squashed tubes. An unresolved issue, then, is whether the mechanism can drive a MST in metallic zigzag SWNTs. Experimental measurements and theoretical simulations both show that a MST can be achieved more easily in metallic zigzag nanotubes than armchair nanotubes,[5, 6, 7, 8]

but a consistent explanation of the mechanism driving the MST is missing. In this paper, a unified explanation is presented for the MST in SWNTs based on a simple tight-binding model. Simple structural trends based on the tight-binding model are used to explain the MST. First, two different mechanisms that can drive a MST in SWNTs are presented, including i) a difference in the onsite energies of the two sublattices and ii) a difference in the nearest-neighbor hopping integral along the axis and along the circumference. It is shown that only the first mechanism can lead to the MST in armchair SWNTs, while both mechanisms can drive a MST in metallic zigzag SWNTs. It is also shown that it is the second mechanism that drives the MST in squashed metallic zigzag SWNTs. Last, it is pointed out that the effects of the two mechanisms are unified: both make the two original equivalent sublattices *physically* distinguishable. In general, the distinction of the two sublattices is the mechanism that drives a MST in any metallic SWNT. This is also the case for a graphene monolayer, but, incidentally,

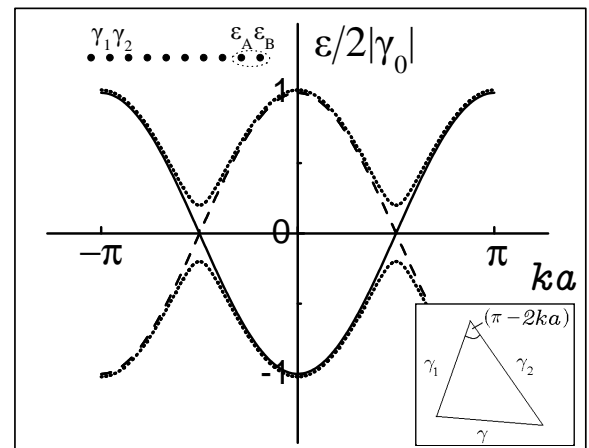


FIG. 1: Solid line: the energy dispersion relation of the one-dimensional lattice system. Dotted line: the energy dispersion relation of the system shown in the left-top corner. Lower right inset: the relationships between γ , γ_1 , and γ_2 .

not the case for a graphene bilayer. This illustrates a key difference between a SWNT and a graphene bilayer.

First, a tight-binding model of a one-dimensional lattice system is considered. The energy dispersion relation of the system, illustrated as the solid line in Figure 1, is a simple cosine function given by

$$\varepsilon - \varepsilon_0 = 2\gamma_0 \cos(ka),$$

where, ε_0 is the onsite energy, γ_0 is the nearest-neighbor hopping integral, k is the one-dimensional wave vector, and a is the lattice constant. For the case in which the bands are half filled, the Fermi energy of the system is ε_0 , and the curve of the energy dispersion relation continues at the Fermi energy, so the system is metallic.

Now, if the one-dimensional system includes two sublattices with different onsite energies ε_A and ε_B , as shown in the left-top corner of Figure 1, then the energy dispersion relation of the system can be expressed as

$$\varepsilon - \varepsilon_0 = \pm\{\Delta^2 + (2\gamma_0 \cos ka)^2\}^{1/2},$$

where, $\varepsilon_0 = (\varepsilon_A + \varepsilon_B)/2$, $\Delta = |\varepsilon_A - \varepsilon_B|/2$. This is plotted in Figure 1 as the dotted line. It can be seen that an energy gap (with value 2Δ) is open near the Fermi energy ε_0 , so the system is semiconducting. From the two cases in this model, it is apparent that a difference in the onsite energies of the two sublattices leads to a MST.

Next, another mechanism leading to a MST in the one-dimensional system is examined: different values of the nearest-neighbor hopping integral. It is assumed first that the two nearest hopping integrals are changed to γ_1 and γ_2 , as shown in the left-top corner of Figure 1, while the onsite energies are kept as ε_0 . The energy dispersion relation of the system is then:

$$\varepsilon - \varepsilon_0 = \pm\gamma,$$

$$\gamma = (\gamma_1^2 + \gamma_2^2 + 2\gamma_1\gamma_2 \cos 2ka)^{1/2},$$

where γ and γ_1, γ_2 can be treated as the three sides of a triangle, as shown in the right-bottom inset of Figure 1. To get $\gamma = 0$, the two conditions: $2ka = \pi$ and $\gamma_1 = \gamma_2$, must be satisfied. So, if the two hopping integrals γ_1 and γ_2 become too different, γ will not be zero no matter what value k is. Then the energy dispersion relation of the system will not be continuous at the Fermi energy ε_0 . An energy gap (with value $2|\gamma_1 - \gamma_2|$) will open near the Fermi energy ε_0 so the system will be semiconducting.

From the above discussion, two mechanisms that can drive a MST in the one-dimensional lattice system are identified: i) a difference in the onsite energies of the two sublattices and ii) a difference in the nearest-neighbor hopping integrals. Furthermore, it can be said that the effect of both mechanisms is to make the two original equivalent sublattices *physically* distinguishable. Applying the same exercise to SWNTs, it is found that only the first mechanism can lead to a MST in armchair SWNTs,

while a MST can be achieved by either mechanism in metallic zigzag SWNTs.

It is well-known that a graphene sheet is metallic. Here the processes of wrapping a graphene sheet into a nanotube and then squashing it are considered. As shown in Figure 2b, the curvature due to the wrapping will reduce the $pp\pi$ overlap between the nearest-neighbor carbon atoms to the original $\cos^2 \alpha$;[9] at the same time, the σ orbital and π orbital between the nearest-neighbor carbon atoms will not be normalized. These two changes lead to different nearest-neighbor hopping integrals along the axis and the circumference. On the other hand, as shown previously,[4] structural perturbations can also introduce new interactions between the atoms in one sublattice, to distinguish from those in the other sublattice, which is equivalent to assigning different onsite energies to the two sublattices, as is the case in Boron-Nitride nanotubes.[10] So, with the structural perturbations, the system shown in Figure 2a will not be a graphene sheet any longer, and it is assumed the two sublattices have different onsite energies ε_A and ε_B , and nearest-neighbor hopping integrals along the x and y directions given by γ_x and γ_y , respectively. Thus, the energy dispersion relation of the system can be expressed as:

$$\varepsilon(k_x, k_y) - \varepsilon_0 = \pm\{\Delta^2 + \gamma^2\}^{1/2},$$

where, k_x and k_y are the wave vector components along

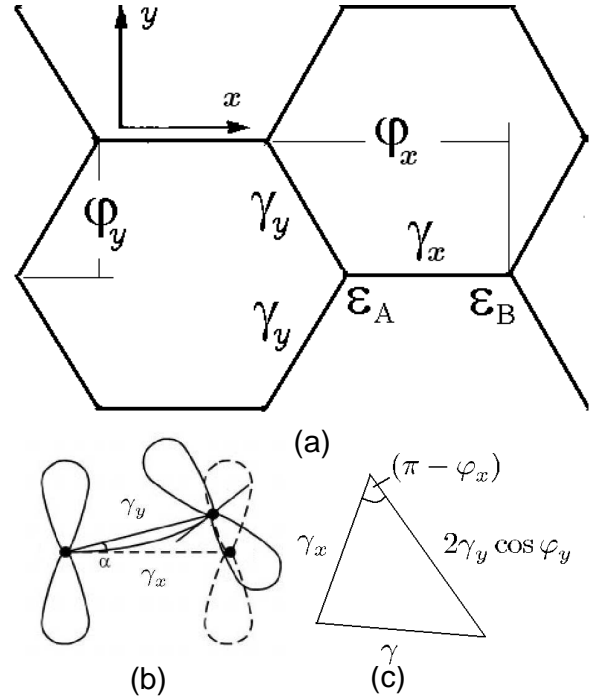


FIG. 2: (a) The graphene sheet-like structure with different onsite energies and nearest-neighbor hopping integrals. (b) The difference between γ_x and γ_y due to the curvature effect. (c) The relationships between γ , γ_x , and $2\gamma_y \cos \varphi_y$.

the x and y directions, and

$$\varepsilon_0 = (\varepsilon_A + \varepsilon_B)/2, \Delta = |\varepsilon_A - \varepsilon_B|/2,$$

$$\gamma = (\gamma_x^2 + 4\gamma_y^2 \cos^2 \varphi_y + 4\gamma_x \gamma_y \cos \varphi_x \cos \varphi_y)^{1/2},$$

φ_x and φ_y are half of the phase increments between the nearest-neighbor carbon atoms which belong to the same sublattice along the x and y directions, as shown in Figure 2a, and $\varphi_x = \sqrt{3}k_x a/2$, $\varphi_y = k_y a/2$.

From the energy dispersion relation, to keep the system metallic, two conditions must be satisfied: $\Delta = 0$ and $\gamma = 0$. Breaking of either condition will lead to a MST. Thus, if the two sublattices have different onsite energies then $\Delta \neq 0$, and a MST can be achieved in not only the armchair SWNTs, but also in all metallic SWNTs and even in the graphene monolayer.

The other condition is that $\gamma = 0$. In fact, as shown in Figure 2c, γ can be treated as one of the sides of a triangle, where the other two sides are γ_x and $2\gamma_y \cos \varphi_y$. So, the condition $\gamma = 0$ can be divided into two conditions: $\varphi_x = \pi$ and $2\gamma_y \cos \varphi_y = \gamma_x$. In the process by which a graphene sheet is wrapped into a SWNT it is found that $\varphi_x = \pi$ can be satisfied in both armchair SWNTs and zigzag SWNTs. For armchair SWNTs, though, the hopping integrals $\gamma_y \neq \gamma_x$ due to the wrapping and squashing. The φ_y can take any value near $\pi/3$ continuously

as the restricted condition is applied on x direction. So the condition $2\gamma_y \cos \varphi_y = \gamma_x$ can always be satisfied. Thus, a difference in the nearest-neighbor hopping integral along the axis and the circumference can not drive a MST in armchair SWNTs.

However, for zigzag SWNTs, the system is restricted in y direction, and φ_y can only take certain discrete values. As a rough approximation, it can be assumed that $\gamma_y = \gamma_x$ holds when a graphene sheet is wrapped into a SWNT. Thus, the condition $2\gamma_y \cos \varphi_y = \gamma_x$ changes to $\cos \varphi_y = 1/2$, so φ_y can only be $\pm\pi/3$. This is the reason for the well-known result that zigzag $(n, 0)$ SWNTs are metallic only when n is a multiple of 3. (In fact, as mentioned above, during the process in which a graphene sheet is wrapped into a SWNT, it is impossible to maintain $\gamma_y = \gamma_x$. So even when n is a multiple of 3, there is a very narrow energy gap near the Fermi energy of zigzag $(n, 0)$ SWNTs, as shown in Figure 3a.) For metallic zigzag SWNTs, when $\gamma_y \neq \gamma_x$ due to the squashing, the condition $2\gamma_y \cos \varphi_y = \gamma_x$ can not be satisfied through adjusting φ_y , as φ_y can only take certain discrete values. Thus, a MST is induced.

Now these results are demonstrated numerically by simulating the squashing of a zigzag (12,0) SWNT, as shown in Figure 3. To squash the tube, simulations are carried out in which two identical tips with a width of $d_x = 5.0 \text{ \AA}$ are used to press the tube symmetrically about its center in the $\pm y$ direction, as shown in Figure 3b. The tips are assumed to be rigid and to contact the nanotube through a hard-wall interaction. The simulations, for both structural optimization and calculation of electronic transport property, are performed using a four-orbital tight-binding (TB) method, the details of which are reported in previous work.[4] The typical conductance curve of a perfect zigzag (12,0) SWNT is shown in Figure 3a. As mentioned above, a very narrow gap is found near the Fermi energy. When the tube is squashed into an elliptical shape, as shown in Figure 3b, a considerable gap can be found near the Fermi energy, indicating that a MST takes place. But to drive a MST in armchair SWNTs requires squashing of the nanotube into a dumbbell shape so that the opposite walls interact. So a MST can be achieved more easily by squashing metallic zigzag SWNTs than by squashing armchair SWNTs.

Last, it is emphasized that the effect of both of the two mechanisms is to make the two original equivalent sublattices *physically* distinguishable, as is the case in the one-dimensional lattice system. In fact, the two sublattices in a graphene sheet or in a SWNT are originally topologically distinguishable. The *physical* distinction means that the two sublattices are ‘felt’ differently by the conducting electrons, which leads to a MST. The first mechanism, the different onsite energies, clearly renders the two sublattices physically distinguishable. And the other mechanism, the difference in nearest-neighbor hopping integral along the axis and the circumference, also makes the sublattices distinguishable, in the following way. The condition $2\gamma_y \cos \varphi_y = \gamma_x$ in a graphene sheet

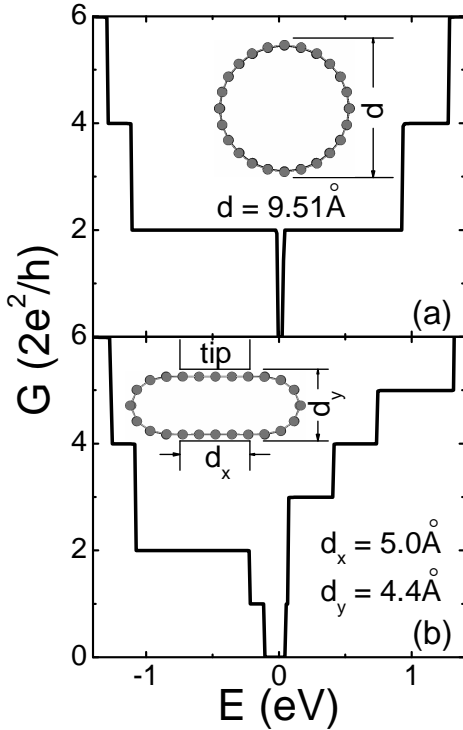


FIG. 3: Conductances of various nanotube structures, which are shown as the insets. E is the energy of injected electrons, and the Fermi energy of an ideal zigzag (12,0) nanotube is taken as zero.

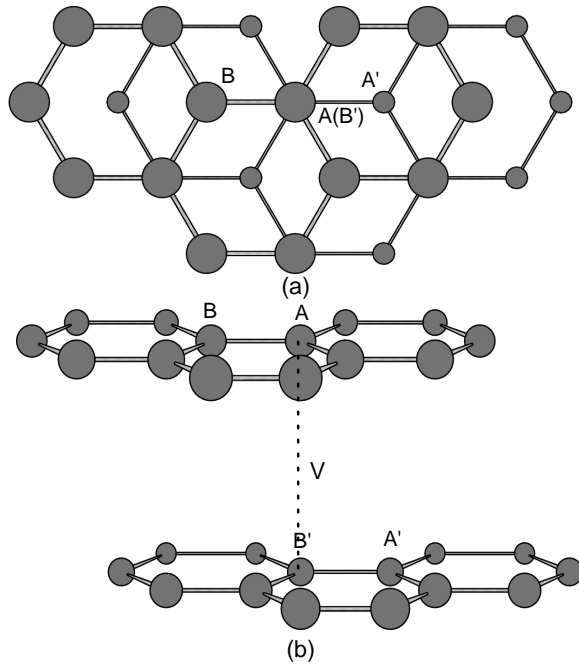


FIG. 4: The graphene bilayers with new interaction introduced between the sublattices A and B'. (a) top view and (b) side view.

can be understood to enforce the equality of the hopping integrals along the x direction (the axis direction of zigzag SWNTs). When the condition can not be satisfied due to the different between γ_x and γ_y , the equality is broken, which leads to the *physical* distinction of the two sublattices, as in the one-dimensional lattice system. But for armchair SWNTs, along the axis direction (y direction), the equality of the hopping integrals can always be satisfied. Thus, the second mechanism can not drive a MST in armchair SWNTs. As an aside, it might be concluded that the *physical* distinction between the two sublattices is a general mechanism which can drive a MST in any metallic SWNTs or even in the graphene layers. But while it can drive a MST in a metallic SWNT, it can not drive a MST in graphene bilayers. For example, as

shown in Figure 4, a new interaction V is introduced between the sublattices A and B' of the graphene bilayers. Clearly, in each layer, the two sublattices are *physically* distinguishable. The energy dispersion relation of the bilayer system can be expressed as:

$$\varepsilon - \varepsilon_0 = \frac{\mp V \pm \sqrt{V^2 + 4\gamma^2}}{2},$$

$$\gamma^2 = \gamma_0^2 (1 + 4\cos^2 \varphi_y + 4\cos \varphi_x \cos \varphi_y),$$

where ε_0 is the onsite energy of the carbon atoms in the graphene bilayers and γ_0 is the nearest-neighbor hopping integral. In fact, $\varepsilon - \varepsilon_0 = \gamma$ is the energy dispersion relation of a graphene monolayer. A graphene monolayer is metallic, so γ can get the value 0 with given value of $\varphi_x = \pm\pi$ and $\varphi_y = \pm\pi/3$. Then, at the same time, for the bilayer system, $\varepsilon - \varepsilon_0 = 0$. This indicates that the system is still metallic and that no MST is achieved. The results show the difference between SWNTs and graphene bilayers.

In summary, the two mechanisms which induce the MST in metallic SWNTs, i) a difference in the onsite energies of the two sublattices, and ii) a difference in the nearest-neighbor hopping integral along the axis and the circumference, are theoretically analyzed through a simple tight-binding model. The results prove that the MST can be achieved more easily in metallic zigzag SWNTs than in armchair SWNTs; only the first mechanism can lead to the MST in armchair SWNTs, but both mechanisms can drive the MST in metallic zigzag SWNTs. Furthermore, the effects of the two mechanisms are essentially the same: to make the two original equivalent sublattices *physically* distinguishable. This is the general mechanism that can lead to a MST in any metallic SWNT and even in the graphene monolayer, but it can not cause a MST in graphene bilayers.

The work is supported by the Ministry of Education of China, the National High Technology Research and Development Program of China (Grant No. 2002AA311153). H.T.J. acknowledges the support of NSF NER Grant DMR 02-10131.

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